A Novel DSC Method to Study Electrode/Electrolyte Reactions

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In a typical differential scanning calorimetry (DSC) experiment, the difference in power required to heat a reference pan and sample pan is monitored as a function of temperature at a fixed temperature sweep rate. This procedure allows for the examination of both exothermic and endothermic events and the determination of their heats of reactions. Typically, DSC sample pans are made of aluminum, but gold, platinum, and stainless steel have been used for specific applications requiring higher temperatures or pressures. To analyze air-sensitive or volatile samples crimped versions of the above holders have been developed. Our experience with crimped aluminum sample pans is that they often leak when a liquid sample is exposed to elevated temperatures during study due to the generation of high pressures.

During the analysis of the thermal stability of various components of lithium-ion batteries, there is the possibility of generating high pressure due to the volatility of the electrolyte solutions [1,2]. To overcome the limitations described above, we have designed a novel DSC sample cell based on welded thin-walled stainless steel tubing [3]. The sample cells can be welded closed in ambient air, or within an inert atmosphere glove box. A large copper heat sink is used during the welding operation to prevent excessive heating of the sample. The thin-walled tubing is relatively inexpensive, the welder is an "off-the-shelf" low power unit, so the entire facility for making such DSC samples is relatively inexpensive compared to other options. Here, we describe the new sample cells, demonstrate that they give reliable measurements for the endotherm associated with the melting of tin and can be used to obtain accurate kinetic information for the decomposition of a thermally unstable compound, di-tert butyl peroxide (DTBP, Figure 2).

Presently many lithium-ion battery researchers are using ARC as an analysis tool [1,2], but many reports can not find the correlation between ARC and DSC. It must be pointed out that the ARC is an **adiabatic** calorimeter and does not represent a “real world” thermal situation [4]. Here we will describe their strengths and weaknesses and show that the same kinetic information can be obtained from both instruments provided that the sample cells are reliable. Finally the analysis of various solvents, electrolyte salts and solutions for use in lithium-ion batteries will be examined with a proposed reaction mechanism for all thermal events, for example see Figure 3.

The new DSC sample cell described here will be a useful tool in examining the thermal stability of various electrolyte solutions and in the analysis of electrode materials reaction with electrolyte.

References

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[3].D.D. MacNeil; S. Trussler; J.R. Dahn, submitted to *Thermochimica Acta* 2001.
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Figure 1. Comparison between conventional hermetic Al DSC pans and the new stainless steel welded DSC pans. A Canadian 10 cent piece showing the famous "Bluenose" is shown for size comparison.

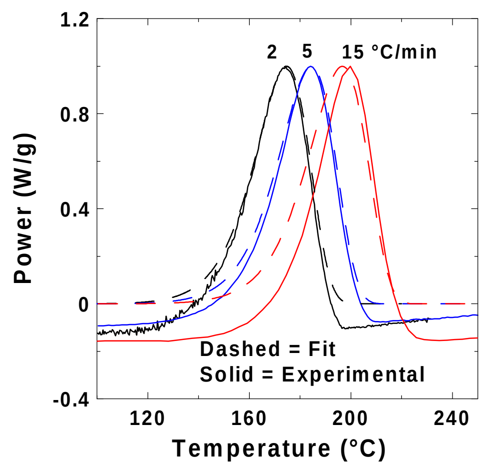

Figure 2. Comparison of calculation (dashed line) and experiment (solid line) for the thermal decomposition of di-tert-butyl peroxide (DTBP) at the indicated heating rates. Evolved power has been normalized to present the results clearly on the same axis

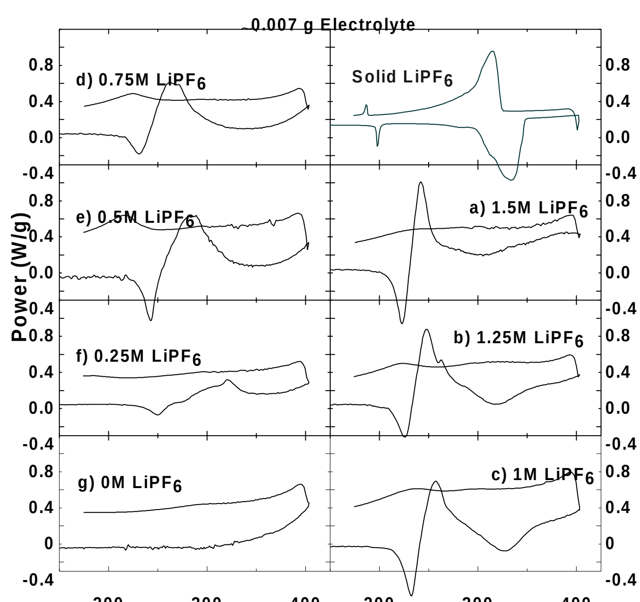

Figure 3. DSC of electrolyte with various concentration of $LiPF_6$ in EC/DEC 33/67 (vol/vol).